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(54) Title: AIR-DRYING ALKYD RESIN AND AN EMULSION THEREOF

(57) Abstract

The invention relates to an emulsion comprising an air-drying alkyd resin dispersed in water having an oil length between 20 and 90 %. The alkyd emulsion is stabilized by salt groups which are chemically attached to the alkyd resin and which are salts of acidic groups having a pKa less than about 3. The invention also discloses the preparation of these alkyd resins, as well as hybrid emulsions of alkyd and acrylate resins.

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AIR-DRYING ALKYD RESIN AND AN EMULSION THEREOF

The invention relates to an air-drying alkyd resin, an emulsion comprising an air-drying alkyd resin and emulsions of an alkyd resin and an acrylate resin.

US-A-4,122,051 discloses an alkyd emulsion being stabilized by neutralizing the free carboxyl groups of the alkyd resin with an amine. The neutralized resin is emulsified in a mixture of water and organic solvent, in which the latter is present in an amount of 10-20 vol.% and is miscible with both the resin and water. In addition, ionic and nonionic emulsifiers are used. A stable emulsion with particles of less than 300 nm is obtained by homogenization. A disadvantage of the alkyd resin emulsion according to US-A-4122051 is that amines, co-solvents and emulsifiers have to be used to stabilize the emulsions. Amines and organic solvents are released upon drying of the alkyd resin and thus impose a burden on the environment. In addition, emulsifiers can have an adverse effect on the hardness of the film, dirt collection tendency and water sensitivity of the coating.

EP-A-267,562 describes emulsions of alkyd resins in which neutralization of the carboxyl groups of methacrylic acid, which had been grafted onto the fatty acid, takes place with amines in order to help stabilize the emulsion. Although use of extra emulsifiers was avoided, these emulsions still contain undesired amines and organic solvents.

In EP-A-02,488, stable emulsions of alkyd resins which were modified with ethylene glycol groups for emulsification were obtained. However, the resultant film was relatively soft. In addition, the description of the composition did not imply that use of amines and organic solvents was avoided.

EP-A-353,477 describes emulsions based on alkyd resins which were stabilized without use of amines but with use of significant quantities of organic solvents and emulsifiers, as well as nitrocellulose. However, according to the examples, at least 50% by volume organic solvent was needed to obtain a stable emulsion.

It is the object of the present invention to prepare stable alkyd emulsions which have good film properties and in which smaller quantities amounts or ideally no amount of amines or organic solvents are needed and in which also the use of non-incorporated emulsifiers has been reduced or can be entirely avoided.

These problems are solved by providing an emulsion of an air-drying alkyd resin having an oil length between about 20% and 90% in water, wherein the emulsion is stabilized by salt groups which are chemically attached to the alkyd resin, and which are salts of strongly acidic groups having a pKa less than about 3.

Emulsions of the alkyd resins according to the present invention are stable and organic solvents, external emulsifiers, and even amines are not required. It is an important advantage of the present invention that the alkyd resins can be directly emulsified in water without use of these undesired stabilizers.

Other important advantages of the present invention are the excellent drying properties and the excellent mechanical stability of the emulsions.

The air-drying alkyd resins according to the present invention can also be mixed with alkyd resins and next emulsified without addition of an external emulsifier. The mechanical stability of the resulting emulsions is excellent.

Generally, between 0.1 and 100 meq of salt groups are present per 100 grams of alkyd resin. Preferably, more than about 0.5 meq, and more preferably, more than about 1.5 meq of salt groups are present per 100 grams of alkyd resin in order to obtain a stable emulsion.

There are preferably fewer than 40 meq of salt groups, per 100 grams of alkyd resin so that the sensitivity towards water in the final film is as low as possible.

The salt groups are salts of acidic groups having pKa's less than about 3. Such acidic groups are generally derived from sulphur or phosphorus.

The acidic groups preferably have a pKa less than about 2. For example, sulphonic acid, phosphonic acid, phosphinic acid, sulphuric acid and phosphoric acid groups can be used.

It has been found to be readily possible, using salts of strongly acidic groups, to obtain stable emulsions with, for example, a pH of between 2 and 10, preferably between 2.5 and 8, in particular between 3 and 8. The fact that these emulsions are less basic is of great advantage because the emulsion is less corrosive while the emulsion itself is highly stable. The emulsions according to the state of the art are generally brought to a pH of 9-11 with the aid of amines in order to obtain sufficiently stable emulsions.

The emulsion according to the invention can contain minor amounts of organic solvents, amines and/or non-incorporable emulsifiers, although use of these stabilizers is generally not needed.

A further advantage of the alkyd resin emulsion according to the invention is the fact that a wide variety of oil lengths is possible with the present system. The alkyd resin can be a long oil alkyd having an oil content (i.e. oil length) of about 60-90%, a medium long oil alkyd, having an oil length of about 40-60%, or a short oil alkyd having an oil length of about 20-40%.

Emulsions of alkyd resins with medium-to-long oil lengths of about 20-90% are often used in air-drying systems without the combination with other resins and cured at ambient or slightly elevated temperatures.

The alkyd resins described in the present invention can be used in paint compositions that, in

addition can contain pigments, fillers, siccatives, additives, or mixtures thereof, and are suitable for many of the usual applications of alkyd resin paints, as known to those skilled in the art.

The alkyd resin emulsion according to the invention can be prepared by mixing the present alkyd resin with water and emulsifying until an emulsion has been obtained having a desired particle size. The emulsion generally has particles with a number-average particle size less than about 1,000 nm and preferably less than about 500 nm, more preferably less than 400 nm. Smaller particles are preferred because these generally give a more stable emulsion. However, more energy is required to obtain smaller particles, so the number-average particle size is generally greater than 50 nm and preferably greater than 100 nm.

An emulsion of the alkyd resin having small particles is generally obtained by first preparing a so-called pre-emulsion by mixing the alkyd resin, which generally contains no solvent, with water using a high-speed agitator. Usually, the pre-emulsion has alkyd resin droplets with a size of 1-50 μm. The pre-emulsion is then emulsified further using a high-pressure homogenizer, such as for example a Nanojet® (Nanojet Engineering GmbH) or a microfluidizer (see for example US-A-4533254 or US-A-4908154). Other high-pressure homogenizers, membrane sonolators or ultrasonificator are also suitable as emulsifying equipment.

Alkyd emulsions with alkyd resins with salt groups attached to the backbone can be prepared in various ways.

It is possible to prepare alkyd resins having acidic groups with a pKa less than 3 and emulsifying this to obtain an emulsion with a resin containing salt groups. Alt rnatively, alkyd resins in which these strongly acidic groups have been converted to salt form can be emulsified.

An alkyd resin with sulfonic acid groups is

described in JP-A-57-185355, the complete disclosure of which is incorporated herein by reference. The alkyd resin is prepared by the initial preparation of a short oil alkyd resin and subsequent esterification of the resin with 5-sulfonic acid-isophthalic acid, and if so desired, with other acids.

Also, an alkyd resin can be prepared as described in, for example DE-A-2,506,156, the complete disclosure of which is incorporated herein by reference. In this preparation, commonly used components for alkyd resins, which are known to those skilled in the art, are used to prepare alkyd resins, which are then sulfonated with sulphuric acid or sulphonic acid.

Alkyd resins with phosphoric or phosphonic acidic groups can be prepared according to, for example, EP-A-131,721, the complete disclosure of which is incorporated herein by reference. According to this process, the alkyd resin can be co-esterified with phosphoric acid. Preferably, however, phosphoric or phosphonic acid is allowed to react with a compound having epoxy groups to form an adduct that is then esterified with either an alkyd resin or the monomers for an alkyd resin.

Furthermore, it is possible to first prepare an alkyd resin having hydroxyl groups and then allow the hydroxyl groups to react with P_2O_5.

For emulsification of alkyd resins having unneutralized, strongly acidic groups, rather than neutralized salt groups, the alkyd resin is preferably emulsified in a basic solution of a metal hydroxide or an amine to form a stable emulsion. However, if the alkyd resin has sulfonic acid groups, a stable emulsion can result without the use of bases. The concentration of base in the water preferably is adjusted so that the resultant emulsion of alkyd r sin has a pH between about 3 and about 8. However, it is possible to use more base than this, and then neutralize the emulsion or, preferably, the pre-

emulsion.

It is preferred to emulsify an alkyd resin having salt groups attached to the backbone in water.

In addition to aqueous emulsions of alkyd resins, another feature of the present invention is alkyd resins having oil lengths between about 20% and about 90% and having salt groups chemically attached to the resin, which are salts of acidic groups having a pKa less than about 3 - but which are in a nonaqueous or neutralised medium rather than an aqueous medium.

These alkyd resins in nonpolar media, such as for example xylene or toluene, have oil lengths between about 20% and about 90%. These alkyd resins have between about 0.1 meq and about 100 meq of salt groups attached to the alkyd resins which are salts of acidic groups having a pKa less than about 3.

The alkyd resins according to the present invention can be prepared by initial preparation of a substantially oil-free alkyd resin using monomers having salt groups. These oil-free resins are subsequently esterified with an oil, fatty acid, or if desired, other monomers to obtain the desired product.

By using monomers having salt groups, it is possible to obtain alkyd resins with less better color development. If the alkyd resin shows discoloration during preparation, minor amounts of a base such as, for example, lithium hydroxide, sodium hydroxide, potassium hydroxide or dimethylaminopyridine and lithiumchloride can be added. The amount of added base is usually between about 0.05 wt.% and about 2 wt% relative to the alkyd resin.

According to this procedure, alkyd resins can be emulsified directly in water without use of other emulsifiers such as amines, organic solvents, or surfactants.

The emulsions of these alkyd resins are practically neutral or slightly acidic, without any pH adjustment. Preferably, these emulsions have a pH between

about 2.5 and about 4. The preferred pH is achieved by emulsifying the alkyd resin having salt groups attached to the backbone in water, wherein the carboxyl groups of the alkyd resin cause the emulsion to have a slightly acidic character. Slightly acidic pH is advantageous because fungus growth will be retarded, and growth can be entirely prevented by adding a small amount of fungicide, if so desired. However, any paint composition ultimately prepared from emulsions of these alkyd resins will generally have a pH between about 6 and about 8.

It is also possible to bring the pH of the emulsion to between about 5 and about 8 with use of a base to neutralize some of the carboxyl groups.

Preferably, alkyd resins having sulfonate or phosfonate groups are used, because these groups are relatively stable with respect to hydrolysis reactions. Particularly preferred is the use of sulfonate groups, because these groups have a pKa less than about 1 therefore very stable emulsions can be obtained.

A review of alkyd resins, their chemistry and technology can be found in, for example, the Encyclopedia of Chemical Technology, third Edition 1978, pages 18-50, (Wiley: New York) under the topic "Alkyd Resins", the disclosure of which is incorporated herein by reference.

Alkyd resins can be prepared by condensation reactions of polyfunctional alcohols, polyfunctional carboxylic acids, and oils or fatty acids derived from the oils.

Polyfunctional carboxylic acids and the corresponding anhydrides can be, for example, phthalic acid or anhydride, isophthalic acid, terephthalic acid, maleic acid or anhydride, fumaric acid, itaconic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, trimellitic acid or anhydride, pyromellitic acid or anhydride, tetrahydrophthalic acid or anhydride, endomethylenetetrahydrophthalic acid or anhydride, cyclohexanedicarboxylic acid, and the like, or mixtures

thereof.

Monofunctional carboxylic acids that are not fatty acids such as benzoic acid or para-t-butylbenzoic acid can be used, in addition to the fatty acids. The polyfunctional and monofunctional acids can also be used in the form of methyl esters, if so desired.

Polyfunctional alcohols can be, for example, pentaerythritol, glycerol, trimethylol propane, glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,2-propanediol, 1,2-butanediol, 1,3-butanediol, neopentyl glycol, polyethylene glycol, polypropylene glycol, bisphenol-A ethoxylated having 2-12 ethylene oxide units, bisphenol-A propoxylated having 2-12 proplyene oxide units. In addition the polyalkylene glycols can also contribute to stabilize the emulsion.

Fatty acids or oils from which fatty acids are derived, as known to those skilled in the art, can be from vegetable or animal sources. Linseed oil, tall oil fatty acid, soybean oil, cottonseed oil, safflower oil, oiticica oil, caraway seed oil, rapeseed oil, coconut oil, dehydrated castor oil, wood oil, vernonia oil, sunflower oil, fish oil, or mixtures thereof, as well as fatty acids derived from these oils, can be used.

Medium-long oil and long oil alkyd resins contain unsaturated and polyunsaturated fatty acid chains for oxidative drying, as known to those skilled in the art.

As known to those skilled in the art, these alkyd resins can be further modified by use of, for example, polyacrylates, polystyrene, polyisocyanates so that urethane groups are obtained, silicone resins, phenol resins, colophony resins, epoxy esters, epoxy resins, or mixtures thereof.

Monomers having acidic groups with a pKa less than about 3 are preferably used in the salt form, and more preferably, in the alkali metal salt form. Suitable

alkali metals include lithium, sodium, and potassium. However, ammonium or alkylammonium groups can also be used as counterion. Furthermore, cations of magnesium, calcium, barium, iron, and other metals can also be used.

Aliphatic and aromatic monomers are suitable as sulfonic acid compounds. Preferably, salts of aromatic sulfonic acid compounds are used. These monomers can additionally have at least one, but preferably two, reactive groups for an esterification reaction. Hydroxyl, carboxyl, or ester groups are preferred for the additional reactive group.

Sulfonic acids, which are preferably converted to the salt form, can be, for example, sulfosuccinic acid (anhydride), 4-sulfophthalic acid or anhydride, 2-sulfoterephthalic acid, 5-sulfoisophthalic acid, 5-sulfodimethoxylate isophthalic acid, 5-sulfosalicylic acid, sulfonated and ethoxylated bisphenol-A, sulfonaphthalene dicarboxylic acid, and the like, or mixtures thereof. Esters of sulfodicarboxylic acids are described in, for example, US-A-2,028,091, the complete disclosure of which is incorporated herein by reference.

Monomers having phosphonic acid groups can be structurally analogous, as known to those skilled in the art, to the monomers carrying sulfonic acid groups, described in the previous paragraph.

As monomers having phosphate groups, hydroxyalkyl ester compounds can, for example, be allowed to react with P_2O_5 to form alkyl ester compounds having phosphate groups.

Monomers with salt groups generally dissolve poorly in the oils or fatty acids used for alkyd resin synthesis. However, use of the acidic form of the monomer during alkyd resin synthesis often leads to undesirable discoloration of the resin. For this reason, the alkyd resins according to the invention are prepared in several steps.

During the alkyd resin synthesis, which can be

carried out with standard procedures known to those skilled in the art, an organic solvent is generally used which forms an azeotrope with water, so that the water formed during the condensation polymerization reaction can be removed by distillation. In addition, esterification catalysts such as for example n-butylchlorotin-(IV)dihydroxide (Fascat®) are generally used.

At the end of the alkyd resin synthesis, which usually is determined from the acid number, any residual solvent is removed, and the alkyd resin is cooled to between about 20°C and 150°C and emulsified in water. The temperature used usually depends on the viscosity of the alkyd resin. For example, a resin having a lower viscosity is easier to emulsify, so in this case, a slightly elevated temperature is generally advantageous.

These alkyd resins having salt groups attached to the backbone generally have acid numbers of less than about 50 mg of KOH per g of resin, and preferably, less than about 20 mg of KOH per g of resin. The acid number is related to the number of carboxyl groups, which have a pKa higher than about 3. An alkyd resin having a low acid number, will positively influence the aging properties. Generally the alkyd resin has an OH number of less than about 100, and preferably, less than about 50. The OH number is generally greater than about 5.

The alkyd resin according to the invention is also very suitable for making so-called 'hybrid emulsions', in which the alkyd resin is combined with another resin such as for example an acrylate resin.

Hybrid emulsions of alkyd resin and acrylate resin are known, for example, from WO 83/00151. According to WO 83/00151 a hybrid emulsion is obtained by mixing an alkyd resin with acrylate monomers and an ethylenically unsaturated emulsifier, which can copolymerize with the acrylat monomers. Disadvantages of WO 83/00151 are that only certain unsaturated emulsifiers can be used and only alkyd resins with short oil lengths were used.

According to EP-A-072979 alkyd acrylate hybrid emulsions were prepared without use of volatile amines by using copolymerizable amines. However EP-A-072979, also does not describe alkyd resins with a medium-long or long oil length.

According to EP-A-083137 alkyd acrylate hybrid emulsions can be prepared by polymerizing acrylate monomers in the presence of a dissolved alkyd resin and an emulsion of the alkyd resin. A disadvantage, however, is that a soluble alkyd resin must be used, so that the water sensitivity of the resultant film is increased.

In the hybride emulsions according to the invention no emulsifier need be used and emulsions can be converted into films having a very low water sensitivity. In addition, although this is not preferred, the hybrid emulsion can also comprise an oil-free alkyd resin.

The hybrid emulsion comprising an alkyd resin and an acrylate resin in water in which the alkyd resin has an oil length of between 0 and 90%, and the emulsion being stabilized by salt groups of an acid, the acid group being attached to the alkyd resin, the salt groups used being the salt of an acid with the acid having a pKa of less than 3. The alkyd resin preferably has an oil length of between about 20 and 90%.

The resin particles in this hybrid emulsion consist of so-called interpenetrating networks of alkyd polymer and acrylate polymer. This is shown by Transmission Electron Microscopy (TEM) analysis of the emulsion particles stained with osmium tetroxide. All particles prove to be homogeneous and gray which indicates the presence of both alkyd and acrylate polymer well-mixed within the particles.

A substantially oil-free alkyd resin having an oil length of less than 5% can be prepared as known to a man skilled in the art using essentially the same polycarboxylic acids and polyalcohols as described previously herein for the preparation of oil-containing

alkyd resin.

The alkyd acrylate hybrid particles can readily be made by mixing acrylate monomers with alkyd resin and emulsifying this mixture in water. This emulsification can be effected in the same way as the emulsification of the alkyd resin itself. It is thus possible to emulsify an acidic resin in a basic aqueous solution or to introduce an alkyd with salt groups into a virtually neutral aqueous phase.

The hybrid emulsion of an alkyd resin and an acrylate resin is preferably prepared by first preparing a pre-emulsion containing alkyd resin and an unsaturated monomer in the presence of customary emulsifiers for emulsion polymerization in water at temperatures less than about 100°C. The pre-emulsion is then passed through emulsifying equipment to obtain a stable emulsion with a desired particle size. An emulsion polymerization is carried out using customary conditions known to those skilled in the art. The emulsion having an average particle size of between for example 50 and 400 mm, can then undergo a radical polymerization, to yield an emulsion with alkyd and acrylate polymers. This polymerization can be carried out continuously or batch wise. In the former case, the homogenized emulsion is slowly added to a reaction containing water or an aqueous solution of any additional emulsifier. In the latter case, the emulsion is charged to the reactor at once. The polymerization is started with the addition of a customary initiator. Emulsion polymerization can also be carried out as a continuous process in, for example, a loop reactor.

The weight ratio of alkyd resin to unsaturated monomer is generally between about 10:90 and about 90:10, and preferably, is between about 20:80 and about 50:50.

The number-average particle size for the pre-emulsion is usually between about 10 μm and about 1,000 μm before treatment in the emulsifying equipment. After treatment in the emulsifying equipment, particle size is

usually between about 50 nm and about 400 nm.

During preparation of the pre-emulsion and before treatment in the emulsifying equipment, water can be added to the solution of the alkyd resin in acrylate monomers. The added water can additionally contain anionogenic emulsifying compounds, although this is not preferred.

Unsaturated monomers can be, for example, mixtures of acrylate monomers and styrene. Preferably, the acrylate polymer has at least 30 wt% acrylate content.

Suitable acrylate monomers include, for example, alkyl methacrylates. Preferably, C_1-C_8 acrylates are used such as, for example, methyl methacrylate, ethyl acrylate, cyclohexyl acrylate, ethyl hexyl acrylate, butyl methacrylate, or mixtures thereof. Preferably, mixtures of styrene, methyl methacrylate, and C_2-C_8 methacrylate are used.

Other suitable unsaturated monomers include, for example, dialkyl maleates; dialkyl fumarates; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl stearate, vinyl laurate, or vinyl versatate; vinyl ethers; vinyl chloride; alkenes such as ethylene, propylene, isobutene, butadiene, vinyl toluene, α-methylstyrene, p-methylstyrene, or methacrylonitrile; or mixtures thereof. Di(C_2-C_8) alkyl maleates, vinyl acetate, acrylonitrile, di(C_2-C_8) alkyl fumarates such as diethylhexyl fumarate, and vinyl esters are preferably used.

The hardness of the acrylate resin depends on which acrylate monomers are selected, as known to those skilled in the art. Usually, the monomers are selected so that the hardness of the acrylate resin of the blend does not differ substantially from the hardness of normal, unblended acrylate resins.

Emulsion polymerization is carried out using catalysts such as, for example, persulfates, hydrogen peroxide, peroxides, and azo compounds. Reducing agents

can be used. The temperature for polymerization is usually between about -15°C and about 100°C, and preferably, between about 20°C and about 90°C. It is necessary to add anti-freeze agents at temperatures below about 0°C. During polymerization, other compounds can be present such as, for example, chain terminating agents like mercaptans and buffers like bicarbonate, as known to those skilled in the art.

The dispersion can optionally contain additional emulsifiers in amounts between about 0.2 and about 10.0 wt%, and preferably, between about 0.5 and about 5.0 wt%, although use of additional stabilizers is not preferred. If additional emulsifiers are used, preferably, anionic or nonionic emulsifiers are used. Suitable examples are salts of alkyl carboxylic acids, alkyl sulfates, alkyl sulfonates, alkyl phosphates, alkyl amines, alkyl aryl sulfonates, alkyl polyethylene glycol ethers, alkyl aryl polyethylene glycol ethers, or mixtures thereof. For optimum emulsification, preferably, mixtures of nonionic and anionic stabilizers are used.

The molar mass of, for example, the acrylate resin does not differ substantially from the molar masses (between about 10^5 and 10^6 Dalton) usually obtained in emulsion polymerization.

The conversion of the ethylenically unsaturated monomers is generally higher than about 90%, preferably higher than about 95%.

The hybrid emulsions according to the invention can readily be used in paint compositions after the addition, if so desired, of pigments, fillers, siccatives and/or additives. The compositions are suitable in usual applications of alkyd-resin-based and/or latex-based paints, which are known to these skilled in the art.

The hybrid emulsions obtained can for example be used as a basis for stains and paints in the do-it-yours lf sector and the construction sector. The alkyd/acrylate weight ratio is then mostly between 25:75

and 75:25.

In the case of alkyd/acrylate weight ratios of between 10:90 and 40:60 the binders can for example be used as a basis for primers for 24-hour systems and dipping primers.

EP-A-548728 relates to an aqueous filler composition which contains a polyester resin derived from dicarboxylic acid containing no sulphonate or phosphonate groups, difunctional monomers containing COOH and/or OH-groups and at least one sulphonate or phosphonate group, a difunctional compound, a higher-functional compound and 0-20 mol% monofunctional carboxylic acid. In contrast to the resins according to EP-A-548728, which relate to polyester resins based on saturated monofunctional carboxylic acids which have to be crosslinked with 10-35 % by weight of a crosslinker, the resins according to the present invention are air-drying alkyd resins.

The invention will be further explained with reference to the following, non-restrictive examples.

Examples I-V

A three-neck round-bottom flask was filled with neopentyl glycol and 5-sodium sulfonate isophthalic acid (SSIPA) in amounts given in Table 1. The flask was equipped with a condenser, a dean-stark collector, a vigreux tube, and a heating jacket. Usually, about 0.5 g of Fascat 4101® as catalyst and about 0.5 g of trinonyl phenylphosphite as antioxidant were used per kg of alkyd resin.

The mixture was heated to about 230°C under a nitrogen flow. After about one hour, the acid number was about 0, and adipic acid was added after cooling to about 150°C. After about two hours of reaction at about 230°C, the reaction product of tall oil fatty acid and trimethylol propane was added, during which time, the contents of the flask were not cooled below about 200°C, and care was taken to keep the contents homogeneously

mixed. During this third stage, xylene was added as azeotropic solvent as soon as the viscosity of the alkyd resin was so high that the water could no longer be readily removed by passing nitrogen through the resin.

After a desired acid number had been reached, which usually was less than 10, the xylene was removed by distillation in vacuo. The resulting alkyd resin was pale yellow and had characteristics given in Table 1.

TABLE 1

Example	I	II	III	IV	V
Composition (pts./wt.)					
neopentyl glycol	133	133	133	133	133
SSIPA	8.5	17	58	84	172
adipic acid	450	447	423	409	363
trimethylol propane	332	332	332	332	332
tall oil fatty acid	884	884	884	884	884
Characteristics					
acid number	18	<10	<10	<10	<10
salt groups (meq/100 g)	1.9	3.9	13	19	37
SSIPA (w/w%)	0.5	1.0	3.5	5.0	10

Examples VI-VIII

Alkyd resins II, IV, and V were cooled to about 140°C and pre-emulsified in water to form an oil-in-water emulsion with particle size of about 1-25 μm. This pre-emulsion was prepared with use of an IKA ULTRA-TURRAX® T25 dispenser with a stirring speed between about 2,800 and about 24,000 revolutions per minute.

Emulsions VI-VIII were prepared using high-pressure emulsifying equipment (a M110Y microfluidizer) at about 700 bar and about 140°C. In some cases, it was necessary to treat the pre-emulsion twice with the microfluidizer to achieve the desired particle size. The

emulsions of a medium-long-oil alkyd with an oil length of 55% thus obtained proved to be completely stable during storage at room temperature. The pH of these emulsions was between about 2.8 and about 2.9.

After addition of siccatives, the emulsions were poured onto a glass plate, and the hardness after one day was determined using a BYK König hardness meter. The results are given in Table 2. Hardness is given in (sec): the harder the film, the higher the hardness value.

The above results show that stable alkyd emulsions with excellent paint properties can be prepared without use of amines, organic solvents, or emulsifiers.

TABLE 2

Example	VI	VII	VIII
resin	II	IV	V
water (%)	40	40	40
particle size (nm)[1]	320	205	260
film hardness (sec)	45	50	20

[1]number-average

Examples IX-XI

Alkyd resins I, II and III (400 g) were mixed with 400 g of butyl methacrylate. Afterwards, 800 g of water were added, and the mixture was pre-emulsified at room temperature. Next, the mixture was emulsified in high-pressure emulsifying equipment as described in Examples VI-VIII at room temperature. The particles had a number-average particle size between about 150 nm and about 400 nm. The pre-emulsion was heated to 80°C, and 2,2'-azobisisobutyronitrile was added in three portions of 1 g in three hours. After 6 hours, potassium persulfate was added, and polymerization was stopped at about 95% conversion.

The hybrid emulsion particles were observed by TEM analysis after staining with osmium tetroxide. The particles were homogeneously grey, which indicated the alkyd and acrylate resins in the particles were well-mixed.

The emulsions contained about 2.5 wt% coagulum and were stable at a pH of about 6. Results for hardness and particle size are listed in Table 3.

Examples IX-XI show stable hybrid emulsions can be prepared.

TABLE 3

Example	IX	X	XI
alkyd	I	II	III
particle size (nm)	364	228	176
film hardness (sec)	7	14	n.d.

Example XII-XVI

By procedures analogous to those described for Examples I-V, alkyd resins XII-XVI were prepared having acid number less than about 10. Composition and characteristics are shown in Table 4.

TABLE 4

Example	XII	XIII	XIV	XV	XVI
Composition (pts./wt.)					
neopentyl glycol	150	104	295	221	70
SSIPA	14	30	51	55	40
phthalic anhydride(1)		325	653		446
isophthalic acid(1)	375				
adipic acid(1)			730		
pentaerythritol	170	232	310		
trimethylol propane				553	430(2)
tall oil fatty acid	780	800	1470	1474	1145

Characteristics					
OH number	24	58	17	23	20
oil length	60	60	59	56	60
salt grp.(meq/100g)	3.9	8.0	7.4	7.5	7.5

(1)acid added in a second step
(2)214 parts/weight TMP were esterified with neopentyl glycol and SSIPA in a first step.

Examples XVII-XXI

By procedures analogous to those described for Examples VI-VIII, emulsions were made from the alkyd resins prepared in Examples XII-XVI. Results are listed in Table 5.

TABLE 5

Example	XVII	XVIII	XIX	XX	XXI
Alkyd resin	XII	XIII	XIV	XV	XVI
% water	40	40	40	40	40
pH	2.7	2.8	2.9	2.8	2.9
particle size (nm)	290	390	488	415	211
film hardness (sec)	n.d.	50	11	58	20

Examples XXII-XXIV

From alkyd resins XIV, XV, and XVI, stable hybrid emulsions were prepared by procedures analogous to those described for Examples IX-XI. However, methyl methacrylate was used in place of butyl methacrylate in Example XXIV. The results are listed in Table 6.

TABLE 6

Example	XXII	XXIII	XXIV
alkyd resin	XII	XV	XVI
particle size (nm)	540	193	445
hardness (sec)	38	7	55

Example XXV-XXIX

Alkyd resins having an acid number less than about 10 were prepared by procedures analogous to those used in Examples I-V . SSIPA was esterified in a first step with 1,6-hexanediol, neopentyl glycol, and ethylene glycol. Composition and characteristics of the alkyd resins are listed in Table 7.

TABLE 7

Example	XXV	XXVI	XXVII	XXVIII	XXIX
Composition (pts./wt.)					
1,6-hexanediol			90		
neopentyl glycol	80	160		60	160
ethylene glycol				60	
SSIPA	36	36	28	30	50
phthalic anhydride	330		296		435(1)
adipic acid		210		400	
isophthalic acid		210			
pentaerythritol	275	275	210	130	275
tall oil fatty acid	1200		840	850	
soybean fatty acid		1200			1000
trimethylol propane				100	
Characteristics					
OH number	24	40	24	20	42
oil length	70	66	64	60	58
salt groups (meq/100 g)	7.5	7.0	7.6	7.6	10.4

(1) together with phthalic anhydride, 4 g of $LiOH.H_2O$ were added, causing the resin to retain a very light color.

Examples XXX-XXXIII

From alkyd resins XXV and XXVII-XXIX, emulsions were prepared by procedures analogous to those described in Examples VI-VIII. The results are listed in Table 8.

TABLE 8

Example	XXX	XXXI	XXXII	XXXIII
resin	XXV	XXVII	XXIII	XXIX
particle size (nm)	449	174	n.d.	152
film hardness (sec)	18	20	27	6

Examples XXXIV-XXVII and Comparative Example A

Alkyd resins were prepared by procedures according to Examples I-V.
Compositions and characteristics of the alkyd resins are listed in Table 9.

TABLE 9

Example	XXXIV	XXXV	XXXVI	XXXVII	A
Composition (pts./wt.)					
neopentyl glycol	160	160	160	160	160
SSIPA	24	75	12	50	-
phthalic anhydride	450	75	456	435	465
pentaerythritol	275	275	275	275	275
soybean fatty acid	1000	1000	1000	1000	1000

Characteristics					
OH number	41	41	41	41	41
oil length	58	58	58	58	58
SO_3^- groups (meq/100 g)	5.0	15.5	2.5	10.4	-
The particle size of emulsions of these alkyd resins (nm) was:	399	380	176	232	232

The mechanical stability was defined by the following procedure. The emulsion was diluted to 20% solids content of which 50 ml was placed in a cylindrical flask with a diameter of 7 cm. The emulsion was stirred for 15 minutes with a flat circular stirrer with a diameter of 6 cm at 7,000 rpm or 9,000 rpm. Subsequently the height of the foam layer was measured. After one day the amount of precipitation was taken for the stability. Complete stable emulsions, without any precipitation were given the valuation "3". Emulsions that were still white, but showed some amount of precipitation were given the valuation "2". A "1" was given to emulsions that were completely separated into distinct alkyd and water phases.

TABLE 10

Alkyd emulsion according to	XXXIV	XXXV	XXXVI	XXXVII	A
7000 rpm;					
mm foam	35	37	14	29	51
stability	3	3	3	3	1
9000 rpm;					
mm foam	47	23	12	30	50
stability	3	2	3	3	1

Examples XXXVIII-XXXXII

From alkyd resins XXV and XXVII-XXIX, hybrid emulsions were prepared by procedures analogous to those

described in Examples IX-XI. However, styrene was used in place of butyl methacrylate in Example XXXX. The results are listed in Table 11.

TABLE 11

Example	XXXIV	XXXV	XXXVI	XXXVII	XXXVIII
resin	XXV	XXVII	XXVII	XXVIII	XXIX
part. size (nm)	380	363	387	n.d.	n.d.
hardness (sec)	n.d.	60	29	18	17

Example XXXXIII

An oil-free alkyd resin was prepared by esterifying 660 parts by weight neopentyl glycol, 35 parts by weight SSIPA, and 0.8 parts by weight catalyst in a first step, and subsequently, esterifying this product further with 200 parts by weight trimethylol propane, 700 parts by weight isophthalic acid and 400 parts by weight adipic acid. From 200 g of polyester and 600 g of butyl methacrylate, a hybrid emulsion was made with 800 g of water, by procedures analogous to those described in Examples IX-XI. The resultant emulsion had a number-average particle size of 386 nm. From the emulsion, a film was obtained having Konig hardness, after one day, of 31 sec.

While the invention has been described in detail, and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

1. An emulsion comprising an air-drying alkyd resin dispersed in water having an oil length between 20 and 90%, characterized in that the alkyd emulsion is stabilized by salt groups which are chemically attached to the alkyd resin and which are salts of acidic groups having a pKa less than about 3.
2. Emulsion according to Claim 1, characterized in that between about 0.1 and about 100 meq of said salt groups are present per 100 g of said alkyd resin.
3. Emulsion according to either of Claims 1 and 2, characterized in that the acidic groups are derived from sulphur or phosphorus.
4. Emulsion according to any one of the Claims 1-3, characterized in that the pH of the emulsion is between 2.5 and 8.
5. Emulsion according to any one of the Claims 1-4, characterized in that the acidic groups are sulphonic acid, phosphonic acid, sulphuric acid, phosphoric acid, sulphurous acid, phosphorous acid or mixtures thereof.
6. Paint composition substantially based on an emulsion according to any one of the Claims 1-5, wherein the paint composition further comprises pigments, fillers, siccatives and/or additives.
7. A composition comprising an alkyd resin in a nonpolar medium, said alkyd resin having an oil length between about 20% and about 90% and having between about 0.1 and about 100 meq of salt groups per 100 g of said alkyd resin, wherein said salt groups are salts of acidic groups having a pKa less than about 3.
8. Alkyd resin according to Claim 7, characterized in that the acidic groups are derived from sulphur or phosphorus.

9. Alkyd resin according to Claim 8, characterized in that said acidic groups are sulphonic, sulphuric, phosphonic, phosphoric, sulphurous or phosphorous acid groups.
10. Alkyd resin according to any one of the Claims 7-9, characterized in that the alkyd resin has an acid number of less than 20 mg of KOH per g of resin and an OH number of less than 100 mg of KOH per g of resin.
11. A process for preparing an alkyd resin having an oil length between about 20% and about 90% comprising the following steps:
preparing initially a substantially oil-free alkyd resin having salt groups; and
esterifying said oil-free alkyd resin with an oil, a fatty acid, a monomer, or mixtures thereof.
12. A process according to claim 11, characterized in that said salt groups are salts of acidic groups attached to said alkyd resin.
13. A process according to claim 11, characterized in that said salt groups are salts of acidic groups having a pKa less than about 3.
14. A hybrid emulsion comprising an alkyd resin and an acrylate resin dispersed in water, characterized in that said alkyd resin has an oil length between about 0% and about 90% and has attached salt groups which are salts of acidic groups having a pKa of less than about 3.
15. A hybrid emulsion according to claim 14, characterized in that, the oil length of the alkyd resin is between about 20% and about 90%.
16. A hybrid emulsion according to claim 14, characterized in that said oil length is less than about 5%.